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(54) PRINTING AND DYEING PROCESS FOR BLENDED FIBRE FABRICS

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This invention relates to a method of producing solid colored effects on fabrics composed of different type fibres.

It is common in methods now employed for the dyeing and printing of blended fibre fabrics to apply the dyestuff for each fibre type in a separate process. Consequently in considering, for example, a blend of cotton and polyester fibres, one dye is applied to the cotton and another to the polyester in separate processes. Various combinations have been used to colour polyester/cotton blends, for instance, a reactive dye for the cotton and a dispersed dye for the polyester, or a vat dye for the cotton and a dispersed dye for the polyester. This type of multi-stage process dyeing is expensive and difficult to control. Attempts have been made to apply mixtures of reactive and dispersed dyes in a single thermofixed application but have led to very limited success because of the limitations of suitable individual dye selection and because the optimum pH conditions differ for the two types of dyes (reactive dyes need alkaline conditions for fixing, whereas dispersed dyes need acidic conditions). The use of pigment dyes alone, which only coat the surface of the material by bonding to it by a resin or other adhesive material, constitute the nearest known approach to a simple application of one class of color to a blended fibre fabric. However, if pigment dyes alone are used, the fabric colors are unable to withstand abrasive conditions of use as the bond to the smooth polyester fibre, particularly at seams, pleats and creases, is inadequate.

Furthermore all previously known dyeing applications suffer from the necessity of requiring a subsequent washing process after thermofixation, to remove unfixed surplus dyestuff.

It has been found that, by applying dyestuffs in a liquid medium containing a resin binder, fabrics comprising two or more different type fibres can be dyed or printed by thermofixation in a single stage operation which does not necessitate any after washing of the fabric. In particular the invention provides a single stage process for the printing and dyeing of blended fibre fabrics which comprises applying to the fabric

(a) a mixture of dispersed and pigment dyes, or

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(b) a yellow pigment dye, or

(c) an azo dye, or

(d) a mixture of an azo dye and a pigment dye,

in combination with a resin binder, in an all aqueous medium or a water-in-oil or oil-in-water emulsion, drying the fabric after application of the dye and subsequently heating the fabric, at between about 380°F and 430°F, to thermofix the dyestuff onto the fabric.

Dispersed dyes in the context of the process of this invention comprise water insoluble dyes which are introduced as a dispersion or colloidal suspension and which are absorbed into the fibre. Pigment dyes are similarly insoluble but do not normally enter into the fibre but rather are adsorbed onto the surface of the fibre. With the exception of the pigment yellows, the pigment dyes are normally of larger particle size than the dispersed dyes. Neither dispersed nor pigment dyes enter into a chemical reaction with the molecules of the fibre.

In a particular embodiment the invention enables the application of pigment and dispersed type dyes to a fabric comprising a blend of cotton and polyester fibres, in a single thermofix operation, and requires no subsequent after washing since substantially all the dye is fixed. In this process one or more pigment dyes, together with one or more dispersed dyes giving the same shade result, are mixed in a suitable liquid medium containing a resin binder. This dye composition is then applied to the fabric, the fabric is dried and then heat treated to complete the dye application.

The heat treatment fixes some pigment dyestuff to the cotton and some to the polyester. The dispersed dye migrates into the material and "solid" dyes the polyester giving the colored effect on this fibre, and compensates for the lack of durability of the pigment dye on the polyester fibre. Any excess dispersed dye not absorbed by the polyester is fixed, along with the pigment dye, by the resin binder in the application medium. Also some pigment dyestuff (in a varying amount depending upon the particle size of the particular color used) behaves in the manner of a dispersed dye and migrates into the polyester fibres.

In a further embodiment of the invention it has been found that many pigment yellow dyestuffs act like dispersed dyes and dye the polyester. This is because in many pigment yellows the particles are almost as small as in yellow dispersed dyestuffs, and their chemical nature is also similar. Thus when dyeing or printing blend fabrics yellow, by the process of this invention, the dispersed dyes are not required and only pigment yellow dyes need be applied.

The process of this invention also enables the use of azo dyes, in particular naphthol/azo dyes, in the dyeing and printing of blend fabrics in order to obtain solid shades of maximum brightness and strength. Rapidogene (trademark) dyes are an example of the type of naphthol/azo dyes which may be employed for dyeing blended fibre fabrics by the process of this invention. These dyes are marketed in both solution and powder form. The powder form requires water and caustic soda (or other alkali) to make it into solution form before application. The solution type can be directly mixed in. The naphthol/azo dyes are also applied in either an all aqueous medium or a water-in-oil or oil-in-water emulsion, containing a resin binder. In previously known processes where these naphthol/azo dyes have been applied to fabrics constructed of cotton and polyester fibres, considerable difficulty has been encountered in obtaining fixation on the polyester fibres. The present process however gives good fixation on the polyester fibres and enables the naphthol/azo dyes to be successfully used for dyeing and printing blended fibre fabrics. The use of azo dyes in the process of this invention gives shades of a strength and brightness not obtainable by previously known processes.

In a further embodiment of the invention some of the azo dye may be replaced by an appropriate amount of a pigment dye of the same approximate hue. The use of a mixture of an azo dye and a pigment dye results in a coloured product with improved light fastness. A suitable ratio of the amount of azo dye to pigment dye is 1 : 1.

In the process of the invention the selected dyestuff is applied to the fabric in a liquid medium. This medium incorporates the resin binder, which facilitates fixation of the pigment color to both cotton and to polyester fibres, and fixation of any excess dispersed dye which is not absorbed by the polyester fibre. It is because of this fixation of the excess

dispersed dyestuff that no afterwashing is required in the present process. In previously known processes the fabric must be washed after thermofixation to remove the unfixed excess dispersed dyestuff. The preferred binder is BASF "Helizarin Binder Et" (trademark), although other binders (e.g. styrene, acrylic, acrylonitrile resins etc.) may be used in the process of the invention. "Helizarin Binder Et" is preferred because it has excellent fastness to dry cleaning, is not degraded by exposure to light and is one of the few available binders which does not significantly impart a stiff handle to blend fabrics.

The amount of binder may be adjusted to the strength of the individual colors employed and the fastness required in the various consumer products.

In a preferred embodiment of the invention the application medium further includes a fixation accelerator. This compound promotes the dyeing of the polyester and reduces the thermo-fixation temperature. More precisely, it reduces the duration of treatment required for the dyes to penetrate into the polyester fibre. The easement of conditions is advantageous in that the risk of degrading or yellowing the cotton component is thereby minimized, and the tendency of the blend fabric to soften and shrink is reduced.

The choice of such fixation accelerator should be made from the many types and products now in general and well-known employment for this purpose, with discretionary selection being made to choose an accelerator causing no discolouration effects, not necessitating an afterwash and having a dual advantage in that the coloured areas are maintained soft to the touch by reason of partial plasticising of the binder resins. For these reasons phenolic type accelerators are not appropriate. A very suitable agent, to promote fixation and softness in the colcured areas, is dioctyl phthalate.

Arising from the additional function of the accelerator in softening the resin binder in order to give the fabric a soft handle it is important to regulate the amount, for although an increased quantity is advantageous as regards dye fixation on the polyester fibres, too much may make the binder film viscous and tacky.

A preferred application medium also includes the following

additional components,

(a) An emulsifier to aid dispersion of the pigment and dispersed dyestuff and to emulsify the mineral spirit present in the liquid medium. A suitable emulsifier is Dispersol PR (trademark) since this type of polyethylene based product also has a promotional effect in dyeing the polyester. Other types of emulsifiers may be used, but a nonionic type is preferable.

(b) A mineral spirit, which in emulsified form, prevents too much penetration of the dyestuff in printing, and keeps the edges sharp and the colors bright and strong. However, where dye penetration is required, a mineral spirit is

not used, except in those cases where dye migration on drying is to be avoided. Petroleum solvents, such as Varsol and Shellsolv 430 (both trademarks), are examples of suitable light mineral spirits which may be used in the liquid medium.

(c) A thickener for the medium. Suitable thickeners are the cellulose derivative thickeners, the high viscosity alginates and other modified galactomannan products. The preferred thickener is Solvitose OFA (trademark), which as well as acting as a thickener, also stabilises the emulsion and has dispersing properties.

(d) A surface active agent, for example a polyethylene glycol. In particular polyethylene glycol 600 is preferred, since this acts as a humectant, lubricant and plasticiser for the thickener and also improves the dry rubbing fastness of the color.

(e) An additional humectant such as urea. Urea is advantageously used, since, if there are formaldehyde producing resins in the pigment color preparations, it prevents the subsequent formation of any distasteful odour.

(f) A catalyst to promote the polymerisation of the bonding resin, such as di-ammonium phosphate.

Swelling agents may also be incorporated in the application medium, to aid the absorption of the dispersed dye into the polyester fibres.

The above examples of the various ingredients incorporated in the application medium are not to be regarded as in any way limiting. The proportions and the selection of the components of the stock medium for applying the dyestuff to the fabric may be varied and changed within discreet limits according to varying plant conditions and local operating preferences. Variations in the components and their proportions in the liquid medium can be used to produce varying strength shades, and in particular the amount of binder may, where desired, be reduced to create medium or pale tints.

The dispersed and pigment dyes are mixed with the stock medium in proportions depending upon the color and strength required.

The dye solution, containing the stock medium and the dyestuff, is applied to the blended fibre fabric, the fabric is then dried and subsequently

heated to thermofix the dye. Thermofixation is effected at a temperature between about 380°F and 430°F (ambient temperature, the temperature of the cloth may be slightly lower). To obtain good color fastness using dispersed dyes a temperature minimum of 400°F is required, unless a fixation accelerator such as dioctyl phthalate is used, in which case the temperature may be advantageously lowered to 380-385°F. The exact temperature and time for thermofixation are variable and depend upon local conditions such as the efficiency of heat transfer to the fabric on the particular heating machine employed. It has been found to be preferable, when using a fixation accelerator, to heat for three minutes at a machine temperature of 385°F. The use of higher temperatures for a shorter time is not advisable in the application of a mixture of pigment and dispersed dyes on blended fabrics, because the dispersed dye requires time to migrate from both the cotton fibres and the resin binder, into the polyester fibres. However, a higher temperature, for instance 420°F, is possible when the polyester content of the blend fabric is higher i.e. around 75% polyester. It is important that the degree of heat treatment is adjusted to the apparatus or machine used, as excess heating will lead to duller colors. After the heat treatment the dyeing process is complete and no afterwashing is necessary, as no unfixed dye remains.

When naphthol/azo dyes are used instead of a mixture of dispersed and pigment dyes or pigment yellow dyes alone, the process of dye application is followed by acid steam development and then subsequent heat treatment for three minutes at 385°F. The stabilized undeveloped naphthol/azo dyes (e.g. Rapidogenes -trademark) consist of two components combined to develop the insoluble dyestuff moiety in situ on the fibre. This coupling is triggered by the effect of passage through steam and acid vapour i.e. acid steam development or by other application of acid. It is possible to use neutral developing azo dyes and fix by neutral steaming and subsequent heat treatment, but the colors tend to be duller. In some instances neutral developing azo dyes may be fixed and developed by heat treatment alone but results using this process are not very reliable.

The above described process is applicable to many other different blend fabrics of both synthetic and natural fibres besides cotton/polyester

fabrics, and to all weaving constructions.

The process is simple and flexible in operation and provides an economical method of producing abrasion resistant, fast colors on blend fabrics by a reliable technique which does not require any afterwashing. The application of pigment dyes in conjunction with dispersed dyes in a suitable stock medium has never before successfuly been applied, nor was it known that many yellow pigments act like dispersed dyes under suitable application conditions.

The following examples serve to illustrate suitable dyeing recipes according to the present invention but are not to be regarded as in any way limiting. For the purposes of the examples a blend of cotton and of a polyester fibre is considered.

EXAMPLE 1

A suitable liquid medium for carrying the dye to the fabric is:-

Stock Medium

Water	230 grams
Dispersol PR (10% Solution)	20 "
Solvitose OFA	8 "
Polyethylene Glycol 600	2 "
Urea	4 "
Di-ammonium phosphate	4 "
Di-Octyl Phthalate	32 "
Light mineral spirit (Varsol, Shellsolv etc.)	500 "
B.A.S.F. Helizarin Binder ET	200 "
	1,000 grams

The above stock medium represents a printing color recipe; for dyeing application, for instance by mangle pad, the mineral spirit content is reduced to 200 grams or possibly to zero with corresponding make-up with water.

Examples of suitable dyeing solutions comprising the above stock medium and a mixture of pigment and dispersed dyes or a pigment yellow dye

alone, are as follows:-

Colour Obtained	Dye Solution	
Lemon Shade	- Helizarin Yellow GGNT	
Gold Shade	- Helizarin Yellow RRNT	
Orange Shade	- Stock Medium	50 grams
	Helizarin Orange GNT	400 "
	Genacron Brilliant Orange RP paste	550 "
Scarlet Shade	- Stock Medium	100 grams
	Aquaprint Scarlet YDC	500 "
	Genacron Briliant Scarlet GP paste	400 "
Red Shade	- Stock Medium	200 grams
	Helizarin Red BBNT	550 "
	Dispersol Red TB liquid	250 "
Violet Shade	- Stock Medium	150 grams
	Helizarin Violet RNT	500 "
	Palanil Violet 3B liquid	200 "
	Palanil Violet 4REL liquid	150 "
Blue Shade	- Stock Medium	200 grams
	Helizarin Blue BNT	500 "
	Foron Blue SBGL liquid	200 "
	Palanil Blue BGF liquid	100 "
Brown Shade	- Stock Medium	200 grams
	Aquaprint Brown Y	450 "
	Palanil Yellow Brown liquid	250 "
	Palanil Violet 4 REL liquid	100 "
Black Shade	- Stock Medium	100 grams
	Cloprint Black	450 "
	Palanil Black GEL liquid	450 "
Green Shade	- Helizarin Green BNT	

Printing colours are formulated from the above dye combinations according to the strength of shade required e.g.

For strong shades -

Dye Recipe	200 grams
Stock Medium	800 "

For medium shades -

Dye Recipe	70 grams
Stock Medium	930 "

The number of dye recipes is unlimited provided the pigment and dispersed colour components are adjusted to give the same colour result. Then, the various dye recipes may be mixed in any desired proportions to produce intermediate shades to match any desired pattern colours.

The dye recipes illustrated are suitable for blends of cotton and polyester fabrics containing between 66% and 50% of polyester type fibre. For blends with less polyester content the relative amount of pigment dye is increased with corresponding diminution of dispersed component.

EXAMPLE 2

A suitable stock medium for the application of stabilized naphthol/azo dyes (Rapidogene) dyes, to blend fabrics is:-

Stock Medium

Water	240	grams
Dispersol PR (10% Solution)	22	"
Solvitose OFC	8	"
Urea	20	"
Triethanolamine	2	"
Polyethylene Glycol 600	2	"
Di-Octyl Phthalate	32	"
Light mineral spirit (Shellsolv 430)	450	"
Pine Oil	5	"
B.A.S.F. Helizarin Binder ET	220	"
	1,000	grams

Again for dye application the light minerals spirit content is considerably reduced possibly even to zero with corresponding increase of water.

Preferably solution type azo dyes are used and suitable formulations for certain shades are as follows:-

Colour	Dye Solution	
Red Shade	Stock Medium	800 grams
	Printing Red R Solution	200 "
Yellow Shade	Printing Yellow G double solution	200 grams
	Stock Medium	800 "
Black Shade	Stock Medium	750 grams
	Printing Black MAC solution	250 "

Similar formulations may be used for all shades of azo dyes in the stabilized uncoupled condition, for example Rapidogene dyes. It is possible to replace some of the azo dyestuff, for example 50%, by an appropriate amount of a pigment dye of the same approximate hue and this process improves the light fastness of the result.

The use of naphthol/azo dyes in the process of the invention produces solid shades of maximum brightness and strength on blend fabrics and is also advantageous, even on 100% cellulosic fabrics, since no afterwashing is required.

EXAMPLE 3

Powder type azo dyes may be also employed using the same stock medium as that given in example 2, by using the following formulation:-

Cold water	200	grams
Wetting Agent (e.g. Triton X 100, trademark)	0.2	"
Caustic Soda, 50% Solution	50	"
Dye powder	50	" approx.
Disperse and solublise the dye by high speed stirring and then mix also by high speed stirring into -		
Stock Medium (as given in Example 2)	800	"

EXAMPLE 4

The dyes may also be applied in a water-in-oil emulsion system (as opposed to the oil-in-water system given in example 2) by using the following stock medium:-

Stock Medium For Colour Standards

Ethyl Cellulose Solution

Dipentene (Solvenol 1)	750 grams
Industrial Alcohol	40 "
Ethyl Cellulose N 10	125 "
Arlacel C(trademark for sorbitan sesquioleate compound)	60 "
Span 65 (trademark for sorbitan tristearate compound)	25 "

Colour standards are then prepared by mixing the following ingredients with a high speed stirrer in the order shown:-

Recipe For Colour Standards

Light Mineral Spirit (e.g. KB 44.5 -a trademark)	180 grams
Stock Medium (Ethyl Cellulose Solution)	120 "
Oil Phase printing pigment (e.g. Aridye dyestuff)	450 " approx.
Dispersed Dye liquid	250 " approx.

For specific examples, blue and red colour standards are prepared by mixing the following ingredients:-

Blue Standard

Light Mineral Spirit (K.B. 44.5)	180 grams
Stock Medium (Ethyl Cellulose Solution)	120 "
Aridye Blue 2GL paste	450 "
Foron Blue SBGL liquid	250 "

Red Standard

Light Mineral Spirit (K.B. 44.5)	180 grams
Stock Medium (Ethyl Cellulose Solution)	120 "
Sherdye Red B	450 "
Dispersol Fast Red TB liquid	180 "
Water	70 "

These colour standards are then employed in the usual way as straight Oil Phase pigment colours e.g.

Aridye Oil Phase Clear	650 grams
Colour Standard	200 "
Aridye Oil Phase Binder	150 "

After printing the dyes are fixed by heat treatment i.e. three minutes at 385°F in hot air.

In the above examples the following names, Helizarin Yellow GGNT, Helizarin Yellow RRNT, Helizarin Orange GNT, Genacron Brilliant Orange RP, Aquaprint Scarlet YDC, Genacron Brilliant Scarlet GP, Helizarin Red BBNT, Dispersol Red TB, Helizarin Violet RNT, Palanil Violet 3B, Palanil Violet 4REL, Helizarin Blue BNT, Foron Blue SBGL, Palanil Blue BGF, Aquaprint Brown Y, Palanil Yellow Brown, Palanil Violet 4 REL, Cloprint Black, Palanil Black GEL, Helizarin Green BNT, Printing Red R, Printing Yellow G, Printing Black MAC, Aridye Blue 2GL, Sherdye Red B, and Dispersol Fast Red TB are all trademarks.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A single stage process for printing or dyeing a blended fibre fabric comprising a blend of cellulosic fibres and synthetic fibres, which comprises applying to the fabric

(a) a mixture of dispersed and pigment dyes, or

(b) a yellow pigment dye, or

(c) a stabilized azo dye, or

(d) a mixture of pigment and stabilized azo dyes,

in combination with a resin binder, in an all aqueous medium or a water-in-oil or oil-in-water emulsion, drying the fabric after application of the dye, subjecting the fabric to acid treatment when dyestuff (c) or (d) is used, and finally thermofixing the dyestuff by heating the fabric at between about 380 - 430°F, whereby both the cellulosic and synthetic fibres are simultaneously colored, and solid penetration dyeing of the synthetic fibres is achieved.

2. Process as claimed in claim 1 wherein the dyestuff is applied to a fabric comprising a mixture of cotton and polyester fibres.

3. Process as claimed in claim 1 wherein the dyestuff is applied in the presence of a fixation accelerator.

4. Process as claimed in claim 3 wherein the fixation accelerator is dioctyl phthalate.

5. Process as claimed in claim 1 where thermofixation is carried out by heating at about 385°F for about 3 minutes.

6. Process as claimed in claim 2, 3 or 4 wherein thermofixation is carried out by heating at about 385°F for about 3 minutes.

7. Process as claimed in claim 2, 4 or 5 wherein the dyestuff used is a mixture of pigment and dispersed dyes.

8. Process as claimed in claim 2, 4 or 5 wherein the dyestuff used is a yellow pigment dye.

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9. Process as claimed in claim 2, 4 or 5 wherein the dyestuff used is a stabilized azo dye.

10. Process as claimed in claim 2, 4 or 5 wherein the dyestuff used is a mixture of stabilized azo and pigment dyes.

11. Process as claimed in claim 2, 4 or 5 wherein the dyestuff comprises a stabilized naphthol/azo dye alone or in combination with a pigment dye.

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